## R. B. MAC MULLIN ASSOCIATES CONSULTANTS TO THE CHEMICAL INDUSTRIES

CHEMICAL, ELECTROCHEMICAL PROCESS INDUSTRIES

CABLE ADDRESS: MULLINCHLOR



910 HANCOCK BUILDING
45 FALLS STREET 285-7571
NIAGARA FALLS, NEW YORK
ZIP CODE NO. 14303

May 22, 1974

Mr. Edward R. Toth, Jr. General Plant Manager RMI Company P. O. Box 550 Ashtabula, Ohio 44004

EPA Region 5 Records Ctr.

322524

Subject: Chlorine Disposal In Waste Gases From Sodium Plant

At Ashtabula, Ohio

Dear Mr. Toth:

It is our understanding that the Ohio Environmental Protection Agency has requested a statement from your consultants with respect to RMI's proposals for reducing the level of hypochlorite contamination in the sodium plant effluent. That which follows comprises a brief summary of the status of our investigation to date.

The total chlorine emission from the sodium processes at Ashtabula amounts to about 435 lbs./hr. as elemental Cl<sub>2</sub> disposed in varying amounts of air and other impurities. Approximately 50 - 65% of this Cl<sub>2</sub> is clean and available in a reasonable concentration ranging from about 25 to 50 mol % in air. For this portion, Cl<sub>2</sub> recovery utilizing a suitable solvent in an absorption/desorption system is both technically feasible and economically practical.

Provisional plans for recovering this portion of the Cl2 effluent were prepared in our offices under the writer's personal supervision. Prior to making final recommendations, we investigated the efficacy of several different recovery methods including the Diamond Shamrock system utilizing CCl4 as the absorbent. This, and others, have been successfully applied to Cl2 recovery from clean sniff gas at a number of chlor-alkali plants elsewhere.

Due to the unique local conditions existing at Ashtabula, RBMA have recommended use of a proprietary solvent which will afford as good or better recovery efficiencies than can be attained with the other systems investigated. Furthermore, the nature of the solvent proposed is such that by integrating the recovery system with the existing facilities, none of the solvent will leave with the residual air stream. That is, there will be essentially zero contamination in the final effluent gases.

(5)

In the proposed recovery system for the clean gas, we calculate that the stripped air leaving the scrubber will contain 3 lbs./hr. of Cl<sub>2</sub> and 1.0 lb./hr. of our proprietary solvent. The stripped gas will not pass directly to atmosphere, but will be bubbled through milk of lime whereby the Cl<sub>2</sub> is neutralized to CaCl<sub>2</sub> and Ca(CCl)<sub>2</sub>, and the solvent is hydrolized to a hydrated oxide which settles out with the rest of the muds.

Insofar as that Cl<sub>2</sub> which is contained in the dirty cell gas, it should be noted that the Cl<sub>2</sub> concentration in that stream is very dilute and that no known absorption or adsorption scheme exists which can be utilized for Cl<sub>2</sub> recovery excepting at exorbitant expense. As the state of the art now exists, the disposal method now practiced, i.e., reaction with milk of lime (or caustic soda) is the only practicable method we can use. The calculations which follow may increase one's understanding of this problem:

Based on plant records, the estimated average Cl<sub>2</sub> loss from the process as dirty gas is 3600 lbs./day or 150 lbs./hr. For operating health and safety reasons, this amount of Cl<sub>2</sub> is swept out of the operating areas by a stream of dilution air equivalent to about 16,000 SCFM. The gas is highly contaminated with impurities such as sodium oxides, salt fumes (CaCl<sub>2</sub> and NaCl) ferric chloride, silicon tetrachloride, etc. The weight of the dilution air may be estimated as follows:

lbs./hr. air = 
$$\frac{16,000}{359}$$
 x 29 x 60 =  $\frac{77,500 \text{ lbs./hr.}}{0r 2672 \text{ lbs. mols/hr.}}$ 

Cl<sub>2</sub> concentration (aver.) = 
$$\frac{150 \times 100}{77,500}$$
 = 0.2% or

2000 ppm, which is well below economical recovery limits.

It is our considered opinion that any attempt to recover the Cl<sub>2</sub> dispersed with so many impurities in such a large volume of diluent air would be prohibitively expensive and would release large quantities of the solvent itself to the surrounding air.

As we understand it, RMI wishes to continue to absorb the dirty chlorine in milk of lime, settle out the solids and subsequently catalytically decompose the residual Ca(OCl)2 in accord with the following reactions:

$$Ca(OC1)_2 + catalyst \longrightarrow CaCl_2 + O_2$$

It is our opinion that the combination of an absorption system for the clean gas coupled with catalytic decomposition of the OCl ion resulting from neutralization of the dirty gas as described above would represent the best available treatment with current technology. The proposed absorption system will recover 50 - 65% of

the chlorine presently lost for internal process recycling and catalytic decomposition of the residual liquors will reduce the CCl by a factor of at least 30 - 40 times below present levels. Finally, it should be noted that the O2 released by catalytic decomposition of the hypochlorite will appreciably improve the quality of the final effluent. We sincerely believe that implementation of such a program will vastly improve the quality of the effluent generated at the RMI sodium plant.

Yours very truly,

R. B. MACMULLIN ASSOCIATES

Peter P. Beno, P.K.

Senior Partner

PPB/jmt